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LOW FIRING TEMPERATURE CERAMIC FOR MICROCIRCUIT SUBSTRATES

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Methods for fabricating substrates based on low-temperature (firing temperature below 1000°C) ceramic, fired together with a deposited metal coating, are examined. Materials which are promising for use as low-temperature simultaneously fired ceramic (LSC) in the systems B_2O_3 –CaO– SiO_2 and B_2O_3 –CaO– Al_2O_3 are proposed.

Advances in electronics have been made possible by fabricating individual components and entire functional units in electronic devices in the form of small integrated circuits. The need for further miniaturization is forcing researchers to turn to new types of conductors and, in consequence, substrates based on low-temperature ceramic (firing temperatures below 1000°C), fired together with a deposited metal coating, or so-called low-temperature simultaneously fired ceramic (LSC) [1, 2].

A number of methods for fabricating such materials exist. In the most widely used technology a ceramic dielectric is mixed with a low-melting glass. The microstructure of the material after firing consists of ceramic particles in a glass matrix [3, 4]. The overwhelming majority of commercially produced LSC, whose characteristics are presented in Table 1, are produced in this manner [1]. The material has a dense nonporous structure, and its composition and firing conditions are well understood. The advantages of this approach are that it allows for flexible control of the characteristics of LSC and a large choice of oxide systems in which low-melting classes are formed.

However, in a number of cases the presence of an amorphous phase in the material is undesirable, and this makes it necessary to search for new ways to produce LSC. Thus, a different method employs as the initial materials glasses which crystallize during heat treatment [3], thereby making it possible to avoid the presence of an amorphous phase in the material. The literature also contains reports about LSC where a dense structure is formed by firing pre-synthesized phases with low (below 1000°C) crystallization temperature (patents No. 115295 Japan and No. 0058170 USA).

The objective of our investigation is to develop the material characterized by high electrophysical indicators (per-

mittivity 7–9, dielectric loss angle tangent not exceeding 10^{-3}) with firing temperature not exceeding 950°C.

The ternary systems of the type B_2O_3 –CaO– R_mO_n (R_mO_n — SiO_2 , Al_2O_3 , Bi_2O_3 , PbO_2) are promising in this respect. However, because of the need to eliminate harmful chemical compounds from the technological process it is impossible to introduce Bi_2O_3 and PbO_2 , so that the systems Bi_2O_3 –CaO– SiO_2 and B_2O_3 –CaO– Al_2O_3 were chosen as the working systems.

$CaCO_3$, H_3BO_3 , SiO_2 , and Al_2O_3 , which is obtained by roasting aluminum hydroxide, served as the initial materials. The heat-treatment regime for the initial mixtures was determined from DTA data, on the basis of the position of the temperature extrema corresponding to the physical–chemical processes occurring during synthesis. Firing was conducted in the temperature interval 820–920°C.

A eutectic composition with melting temperature 977°C was chosen in the system SiO_2 – B_2O_3 –CaO. Additives to decrease the firing temperature were introduced into this system. The additives were chosen using the procedure described in [5], which relates the temperature at which a liquid phase appears in the multicomponent system studied with the melting temperature of the lowest-melting component and the appearance of a liquid phase in specific binary systems.

RO	Liquid phase appearance temperature, K
CaO	1948
SiO_2	721
MgO	2336
Al_2O_3	749
BaO	1409
ZnO	1601
MnO	1210

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TABLE 1.

Material	Electrophysical properties			CLTE, 10 ^{−6} K ^{−1}	Thermal conductivity, W/(m · K)	Conductor material
	frequency, Hz	permittivity	dielectric loss angle tangent, 10 ^{−3}			
DuPont:						
GreenTape 943	10 ¹⁰	7.5	1.0	6.0	4.4	Ag, Pd – Ag (alloy)
GreenTape 951	10 ¹⁰	7.8	1.5	5.8	3.0	Au, Ag, Pd – Ag (alloy)
Heratape CT2000	2.5 × 10 ⁹	9.1	2.0	5.6	3.0	
Ferro A6-M	10 ¹⁰	5.9	2.0	7.0	2.0	
Kyocera:						
GL550	2 × 10 ⁹	5.6	0.9	5.9	2.0	Ag
GL560	2 × 10 ⁹	6.0	1.7	7.9	1.5	Au, Ag
Nikko AG3	10 ⁶	7.1	3.0	5.5	–	
TDK:						
S39	2 × 10 ⁹	7.5	2.9	6.3	2.9	Ag
T50	2 × 10 ⁹	11.7	3.3	6.4	2.4	
Murata:						
LR	10 ⁶	7.7	5.0 [*]	5.5	2.5	Ag
LA	10 ⁶	8.8	4.0 ^{**}	7.2	3.5	
CeramTec	10 ⁶	7.9	2.0	5.3	–	Ag
CeramTape GC						
ESL:						
41110	10 ⁶	4.5	4.0	6.4	3.0	Ag, Pd – Ag (alloy)
41060	10 ⁶	16.0	2.0	7.55	–	Ag

* Frequency 10^{10} Hz.

** Frequency 6×10^9 Hz.

Evidently, the introduction of SiO_2 or Al_2O_3 gives the lowest temperature. However, introducing additional SiO_2 causes the composition to deviate from a eutectic, so that Al_2O_3 , introduced with the initial components of the eutectic in the amounts of 1, 3, and 5%,² was used as the additive.

Microscopic investigations showed that in the absence of additives the material is composed of crystals of calcium monoborate and monosilicate, and intergrowth of these crystals is observed. The aluminum oxide introduced dissolves either completely (with 1% content) or partially in the amorphous phase which appears, and the residue is uniformly distributed between crystals of the main phases. The remaining closed porosity is explained in this case by the fact that the amount of the liquid phase in the temperature interval considered is too small to fill all pores. Complete crystallization of the amorphous phase does not occur; it remains in amounts up to 5% as interlayers along crystal boundaries. The microstructure of the material, containing various quantities of the additive, is displayed in Fig. 1.

The aluminum oxide additive does not change the character of the synthesis of the eutectic, and powders containing the additive have the same phase composition as samples

without the additive, which is confirmed by data from x-ray phase analysis. Growth of the average density and decrease of the open porosity is observed with increasing roasting temperature, irrespective of the composition.

As the Al_2O_3 content increases in the composition, growth of the average density and decrease of open porosity is likewise observed at the same roasting temperature. However, since in the presence of small quantities of aluminum oxide, the viscosity of borosilicate glasses decreases sharply in the temperature interval $800 - 1000^\circ\text{C}$, the rate of shrinkage and softening up the samples is observed to increase. For introduction of 1% Al_2O_3 , the material sinters to zero open porosity and density close to the theoretical value. A further increase of Al_2O_3 content to 3 and 5% results in softening of the samples. High open porosity with this content of aluminum oxide remains right up to softening.

In connection with the preservation of substantial porosity, the mechanical strength of these samples remains low, though increasing Al_2O_3 content at the same temperature increases the mechanical strength. Naturally, highest porosity is found in ceramic with zero open and minimum closed porosity; the optimal Al_2O_3 content for obtaining dense material without any deformation of the samples is 1%. The

² Here and below — the mass content.

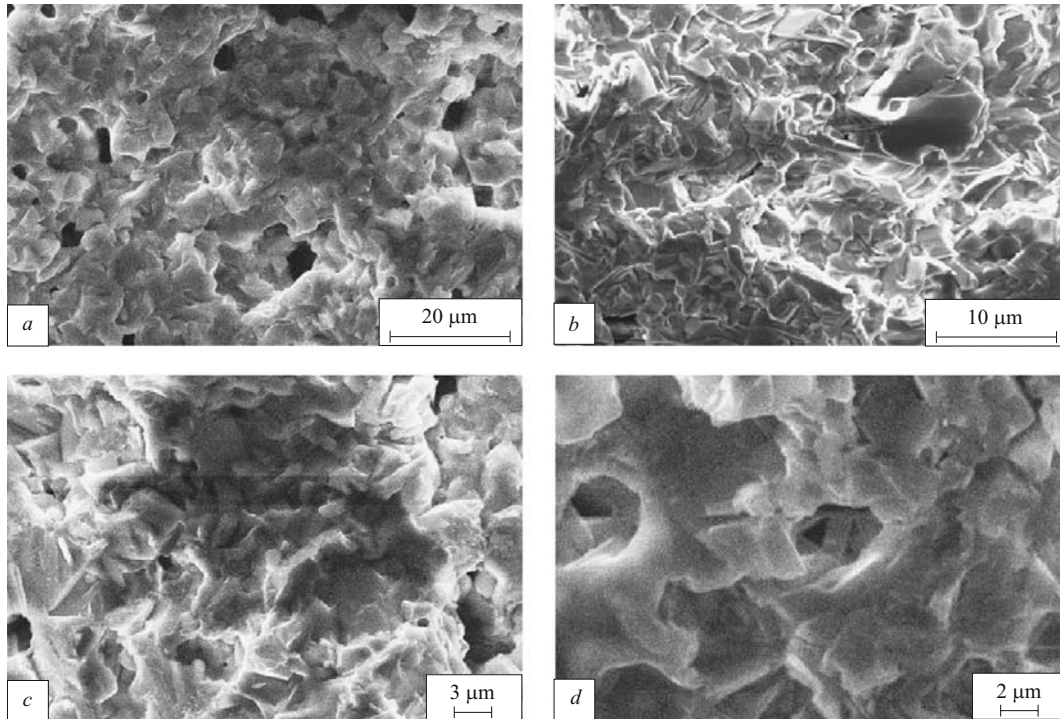


Fig. 1. Microstructure of the ceramic in the system $\text{CaO} - \text{B}_2\text{O}_3 - \text{SiO}_2$ with mass content 0 (a), 1% (b), 3% (c), and 5% (d) Al_2O_3 .

permittivity of this material measured at 1 MHz was 8.2 ± 0.3 , and the dielectric loss angle tangent was 4.3×10^{-3} .

The second system which we are developing, $\text{B}_2\text{O}_3 - \text{CaO} - \text{Al}_2\text{O}_3$, was studied in less detail, so that a number of compositions with a constant ratio $\text{CaO} : \text{B}_2\text{O}_3$ close to the ratio of these oxides at the eutectic point with minimum melting temperature in the binary system $\text{CaO} - \text{B}_2\text{O}_3$ were chosen as the working compositions in it. Aluminum oxide was introduced in amounts 10, 20, and 30%.

Microscopic investigations showed that a multiphase material was formed during firing. Aluminum oxide is present in the bound (calcium bialuminate) and free forms; the content of free Al_2O_3 increases as the fraction of aluminum oxide in the mixture increases. Boron oxide also enters into reaction with calcium oxide, forming mono- and dicalcium borate. The size of the crystals of all phases is $1 - 3 \mu\text{m}$. Interlayers of an amorphous phase of B_2O_3 , whose amount decreases with increasing Al_2O_3 fraction, are observed along crystal boundaries (Fig. 2).

A special feature of these compositions is that after heat treatment of the initial charge the aluminum oxide is not present in a free form, but depending on the amount introduced it is found either entirely in the compound $\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ or it forms a continuous series of salt solutions with binary compounds of calcium borate.

The porosity increases and the average density decreases as the fraction of free Al_2O_3 in the material increases. As temperature increases, a regular change of the ceramic indi-

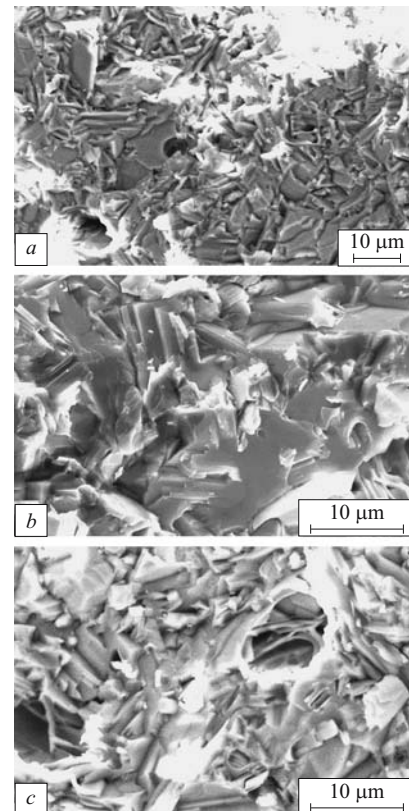


Fig. 2. Microstructure of the ceramic in the system $\text{CaO} - \text{B}_2\text{O}_3 - \text{Al}_2\text{O}_3$ with mass content 10% (a), 20% (b), and 30% (c) Al_2O_3 .

cators occurs for each composition: the density increases and the porosity decreases. But, the composition with 30% Al_2O_3 cannot be fired to a dense state in the temperature interval chosen, while in the presence of 10% Al_2O_3 softening of the samples occurs before the densification process is completed. This behavior is explained by a corresponding change in the amount of the amorphous phase.

The composition with 20% Al_2O_3 , which sinters to zero open porosity and density close to the theoretical value, possesses the best indicators. However, the presence of continuous interlayers of an amorphous phase, whose thickness is comparable to the sizes of the crystals, has a negative effect on the mechanical and electrophysical properties: the bending strength is only 100 ± 15 MPa and the permittivity and dielectric loss angle tangent measured at 1 MHz are 8.1 ± 0.1 and 7.5×10^{-3} , respectively.

In summary, ceramic obtained on the basis of the eutectic composition in the system $\text{Bi}_2\text{O}_3 - \text{CaO} - \text{SiO}_2$ with 1% Al_2O_3 added, whose closed porosity is less than 1%, bending strength 190 ± 40 MPa, permittivity 8.2 ± 0.3 , and dielectric

loss angle tangent 4.3×10^{-3} , and ceramic obtained in the system $\text{B}_2\text{O}_3 - \text{CaO} - \text{Al}_2\text{O}_3$, containing 20% aluminum oxide and having closed porosity of about 2%, bending strength 100 ± 15 MPa, permittivity 8.1 ± 0.1 , and dielectric loss angle tangent 7.5×10^{-3} , are characterized by low firing temperature and are promising as LSC.

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